Shear-Enhanced Crystallization in isotactic Polypropylene. 3. Evidence for a Kinetic Pathway to Nucleation

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Supplementary Information

The exact value of the wall shear strain is not known. The known quantities are the wall shear stress, the duration for which it is applied and the mass extruded during that time. The flow curve of the polymer at a temperature above the nominal melting temperature is also known, and the time-temperature shift behavior of polypropylene can be applied to the melt. Some of the unknowns that prevent quantitative determination of the wall shear strain are the transient behavior upon inception of non-linear shearing and the development of structures that progressively modify the rheology of the sample due to flow-induced acceleration of crystallization.

Here, we give three different estimates of the wall shear strain based on the mass of polymer extruded: a geometical estimate, an estimate based on a Newtonian fluid, and an estimate based on a shear-thinning power-law fluid. All of them assume that steady-state is reached instantaneously and make no attempt to account for the rheology changing with time during shear. The values of the strain, γ_{ge}, reported in our paper are "pseudo"-strains based solely on the geometry of the flow cell. We estimate the strain limit of our instrument as a ratio of the usable length ($\approx$ 5 cm) of the rectangular flow channel to its thickness (0.5 mm) which yields $\gamma_{ge} = 100$. Thus, when a mass equal to all the polymer initially in the flow channel [corresponding to a volume of 5cm x 0.635cm x 0.05cm (length x width x thickness) $\approx$ 190 mg], is extruded, $\gamma_{ge} = 100$. For the same extruded amount, calculating the strain at the wall based on a Newtonian constitutive equation for the flowing melt and assuming that a steady state flow profile is achieved immediately upon imposition of pressure, gives $\gamma_N = 400$. The corresponding wall strain for a power law fluid is $\gamma_{PL} = 200$ x $\frac{n+1}{n}$, where n is the shear thinning index. Capillary

rheometry data at 190°C for the polydisperse polypropylene used in this study gives $n = 0.38$ when fitted to a power law equation. Thus, for extrusion of the volume of polymer specified earlier, $\gamma_{PL} \approx 700$. To avoid ambiguity about the exact value of the strain, we use a well-defined "pseudo"-strain based on the dimensions of our flow channel, γ_{ge}.

The calculation of the wall strain and the wall strain rate is complicated by the phase change (crystallization of the polymer) that occurs during shearing. If the polymer undergoing shear does not undergo a phase change, then it is reasonable to assume that a melt-constitutive equation would describe the flow and that time temperature superposition would hold. Under these conditions, for shearing durations long enough to neglect start-up effects, we expect that the temperature dependence of the average amount extruded per unit time follows the rheological shift factor, a_T, that describes the change in polymer viscosity with temperature. While this appears to be true for high enough temperatures, it is not a good approximation below $T_{cryst} \approx 160$°C (Figure 1-Suppl). This accords well with the WAXD data presented in our paper: for temperatures below 163°C, crystallites are formed rapidly and are can be detected even during shear, while for higher temperatures, crystal growth off the precursors formed during shear happens slowly, dictated by the high T_{cryst} (Figure 3). Therefore, we attribute the deviation from the temperature dependence of a_T at temperatures below $T_{cryst} \approx 160$°C to the formation of crystallites during shear, which increase the melt viscosity significantly and cause the average amount extruded per unit time to fall off much more steeply than expected from a_T. Above 160°C, the growth of crystallites slows down dramatically (see Figure 3) and the average amount extruded tracks the viscosity (hence, a_T).

We have estimated the "pseudo" strain at which the birefringence upturn occurs based on the upturn time, t_u and the average extrusion rate (averaged over a shear duration for which $\gamma_{ge} \geq 50$ and averaged over at least three experiments at each temperature). We

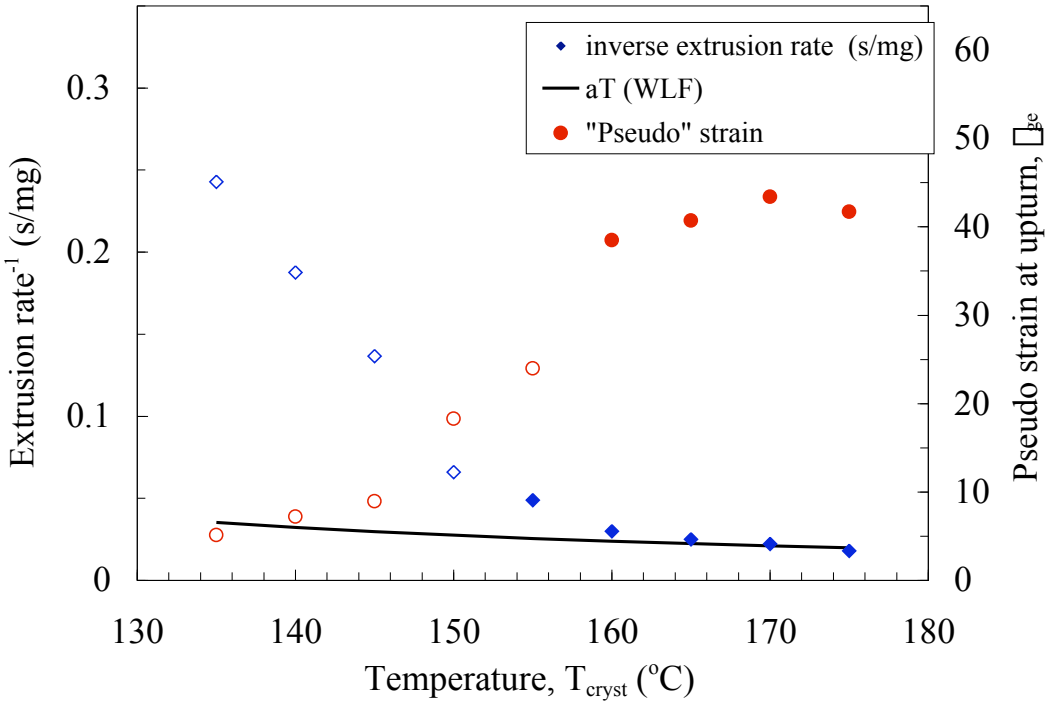

Figure 1: -Suppl: The inverse of the average extrusion rate (blue symbols, left axis) and the "pseudo" strain imposed during shear up to the point of the birefringence upturn (red symbols, right axis) as functions of temperature. At temperatures greater than 160°C, the average rate of polymer extrusion during shearing tracks the WLF time-temperature shift coefficient, a_T (plotted with respect to a reference temperature of 190°C, and multiplied by 0.015 for comparison with the average extrusion rate at high temperatures). The "pseudo" strain at the birefringence upturn, γ_{ge} is approximately constant for temperatures above 160°C.

find that the strain at the upturn is approximately constant ($\gamma \approx 40$, Figure 1-Suppl), for T_{cryst} greater than about 160°C, where the rheology is only marginally modified by the phase change during shearing. We infer that strain at the upturn is nearly constant at this value even at lower temperatures, since the perturbation of the melt rheology occurs at times beyond the upturn: the transient normal stress difference during inception of shear (up to the upturn time) superposes reasonably well with a rescaling of time that tracks the temperature dependence of the melt relaxation time and melt viscosity (inset, Figure 2), suggesting that the reduction in the average rate of extrusion during the entire shearing time is due to structure development during $t > t_u$.